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Spectroelectrochemical Monitoring of Electrode

Reactions by Multiple Specular Reflectance Spectroscopy

by

C. E. Baumgartner, G. T. Marks, D. A. Aikens and H. H. Richtol

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Multiple specular reflection is the basis of a new thin layer spectro-electrochemical cell which does not use optically transparent electrodes, the optical sensitivity of which exceeds that of cells using transparent electrodes by a factor of several hundred. As a result, the ability to detect short-lived intermediates and weakly absorbing species in spectroelectrochemical studies is much improved. Absorbance changes less than 5×10^{-5} absorbance units per electrode reflection are readily observed. A cell 4cm long

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with a 120 μm spacing, operated to give approximately 330 reflections, was used to monitor optically the reduction of methylene blue and the reoxidation of the leuco form at concentrations as low as $5 \times 10^{-7}M$. For both reactions, the absorbance is linear with $\sqrt{t}$ from 10 ms to ca 3 s, and the magnitude agrees well with values calculated from the geometry of the optical path. Amond the advantages of the new technique are greatly increased optical sensitivity and the ability to use electrode materials which are not transparent.

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Spectroelectrochemical Monitoring of Electrode Reactions

by Multiple Specular Reflection Spectroscopy

by

C. E. Baumgartner, G. T. Marks,

D. A. Aikens* and H. H. Richtol*

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BRIEF

A new thin layer multiple specular reflection spectroelectrochemical cell can monitor absorbance changes below 5×10^{-5} absorbance units per electrode reflection.

ABSTRACT

Multiple specular reflection is the basis of a new thin layer spectroelectro-chemical cell which does not use optically transparent electrodes, the optical sensitivity of which exceeds that of cells using transparent electrodes by a factor of several hundred. As a result, the ability to detect short-lived inter-mediates and weakly absorbing species in spectroelectrochemical studies is much improved. Absorbance changes less than 5×10^{-5} absorbance units per electrode reflection are readily observed. A cell 4cm long with a 120 μm spacing, operated to give approximately 330 reflections, was used to monitor optically the reduction of methylene blue and the reoxidation of the leuco form at concentrations as low as $5 \times 10^{-7} \underline{M}$. For both reactions, the absorbance is linear with $\sqrt{t}$ from 10 ms to ca 3 s, and the magnitude agrees well with values calculated from the geometry of the optical path. Among the advantages of the new technique are greatly increased optical sensitivity and the ability to use electrode materials which are not trans-parent.

Techniques for optical monitoring of electrochemical reactions have made it possible to follow optically the concentrations of reactants and products and to detect intermediates (1-10). For study of electrogenerated species in solution, the most widely used methods involve optically transparent electrodes operated in either a transmission or an attenuated total reflectance mode. Specular reflectance has been widely used to detect changes in electrode surfaces, (11-14) and to a limited extent to study electrogenerated solutes(9,10). A thin layer cell technique used by Reilley (9) to monitor stable solution species involved analyzing light reflectance at an opaque platinum electrode. While he recognized the possibility of using multiple electrode reflections, he did not pursue it. A recent review by Heineman (7) summarizes these various techniques.

The major limitation of these techniques, as pointed out by McCreery et al (1), is that the short effective length of the optical path lowers the optical sensitivity and hinders the detection of weakly absorbing or short-lived species. A recent specular reflection technique developed by McCreery et al, in which the analytical beam strikes the electrode at a glancing angle, improves the optical sensitivity for electrogenerated solutes by increasing the path length through the solution layer in the immediate vicinity of the electrode surface. This method is not suited for systems in which a strongly absorbing reactant is transformed into a colorless product, however, because the length of the optical path through the unreacted bulk solution is not negligible in relation to the length through the solution layer adjacent to the electrode.

We report here a method for optically monitoring electrochemical reactions in which the species of interest has a low molar absorptivity or is present in low concentration that is based on multiple specular reflection (MSR) in a thin layer cell. Previous applications of MSR spectroscopy (14,15), most of which have been concerned with studying the electrode surface, have employed electrode

spacings of 0.5 to 2mm, thereby limiting the number of reflections to ca 20 or less. Our technique employs electrode spacings on the order of 100 μm, thus increasing the number of reflections to several hundred. As a result of the increased optical pathlength, the optical sensitivity of an MSR cell is greater than that of a thin layer cell of the same thickness operated in the transmission mode by a factor of several hundred. To illustrate the application of MSR cells, we have used one to monitor optically the electroreduction of methylene blue (MB) and the subsequent reoxidation of the colorless leuco form (LMB) at concentrations ranging from 1×10^{-5} $\underline{M}$ to as low as 5×10^{-7} $\underline{M}$.

THEORY

If the cell in Figure 1 contains a single absorbing species and the light beam traverses it once, A_t, the absorbance at a given time, follows from Equation 1

$$A_t = \epsilon \int_0^\infty C(x,t) d\ell \tag{1}$$

where ϵ represents the molar absorptivity and $C(x,t)$ the concentration profile of the absorbing species as a function of time and distance normal to the electrode surface and $d\ell$ is an increment of pathlength. Replacing $d\ell$ by its equivalent $dx/\sin\alpha$, where α is the angle of the light beam with respect to the electrode surface, yields Equation 2.

$$A_t = \frac{\epsilon}{\sin\alpha} \int_0^\infty C(x,t) dx \tag{2}$$

If the absorbing species is generated by electrode reactions at both electrodes, $C(x,t)$ must be integrated over both diffusion layers. For fluxes controlled by semi-infinite linear diffusion, integration of Equation 2 yields Equation 3

$$A_t = \frac{4\epsilon_P C_R^\circ}{\sin\alpha} \left[\frac{D_R t}{\pi} \right]^{\frac{1}{2}} \tag{3}$$

where the subscript P indicates the product of the electrode reaction, the sub-
script R represents the reactant, C_R^o denotes the bulk concentration of the
reactant, D_R denotes the diffusion coefficient of the reactant and t indicates
the time from the start of the electrode reaction. With a cell thickness of
100 μm, the assumption of semi-infinite linear diffusion is valid for times less
than ca 3 seconds.

For N specular reflections of the light beam, the beam traverses the cell
N + 1 times, which may be approximated as N if N is 50 or more, so that the
total absorbance for N specular reflections is N times the value given by
Equation 3. As Figure 1 shows, d, the distance along the cell associated with
each traverse of the cell by the light beam, is T/tanα, where T is the cell thick-
ness. It follows that the total number of traversals is simply L/d which in terms
of measureable quantities, is L tan α/T. Combining this result with equation 3
yields Equation 4, which defines the total absorbance as a function of time and
measureable physical parameters of the cell.

$$A_t = \frac{4L\epsilon_P C_R^o}{T \cos\alpha} \left[\frac{D_R t}{\pi}\right]^{\frac{1}{2}} \tag{4}$$

Where the absorbing species is the electroactive species instead of the
product of the electrode reaction, the absorbance decreases from an initial
value characteristic of the bulk concentration of the absorbing species and the
cell parameters. Because the solution is originally uniform, the initial absor-
bance is simply the product of the original concentration of the absorbing
species, its molar absorptivity and the pathlength. The latter term is the
product of the number of traversals and the pathlength associated with each
traversal. As has already been shown, the number of traversals is L tan α/T,
and Figure 1 shows that for each traversal, the pathlength is T/sinα. Combining
these results yields the initial absorbance term, and reasoning analogous to
that outlined for Equation 4 yields the time-dependent absorbance term. This

results in Equation 5, where ϵ_R is the molar absorptivity of the electroactive species and the other symbols have the same meanings as before

$$A_t = \frac{L\epsilon_R C_R^{\circ}}{\cos\alpha} - \frac{4L\epsilon_R C_R}{T\cos\alpha}\left[\frac{D_R t}{\pi}\right]^{\frac{1}{2}} \tag{5}$$

Relative to a thin layer cell of the same thickness operated in the transmission mode, typical MSR cells display optical sensitivities that are higher by a factor of several hundred to a thousand. For transient absorbance, the enhancement factor is $2L/T\cos\alpha$, and for the initial absorbance in the absence of applied potential, the enhancement factor is $L/T\cos\alpha$. Thus, an MSR cell 100 μm thick and 4 cm long with the light striking the electrode at 45° enhances the initial absorbance by a factor of 565 and the transient absorbance by a factor of 1130.

The influence of the operating parameters on the measured absorbance also merits brief comment. As expected, increasing the cell length or the angle of the light beam with respect to the electrode surface increases both the transient absorbance and the initial absorbance by increasing the number of times the beam traverses the cell. Also, for a given angle, Equations 4 and 5 show that decreasing the cell thickness increases the transient absorbance, but Equation 5 shows that it has no effect on the initial absorbance. As can be inferred from Figure 1, the optical pathlength per reflection is directly proportional to the cell thickness, but the number of reflections is inversely proportional to the cell thickness, so that the total length of the optical path is independent of the cell thickness. Hence, when the concentration of the absorbing species is uniform, the total absorbance does not depend on the cell thickness. On the other hand, during electrolysis under semi-infinite linear diffusion control, the number of reflections remains inversely proportional to the cell thickness, but the length of the optical path through the diffusion layer per reflection is independent of the cell thickness. As a result, the total path length through the diffusion layer

and the magnitude of the transient absorbance term are inversely proportional to the cell thickness.

EXPERIMENTAL

A cross sectional schematic diagram of the MSR cell is in Figure 1. The two specular electrodes are front surface gold mirrors with an undercoating of titanium to improve the adhesion of gold to the glass (Mellis Griot Co., Irvine, CA). On each end of one mirror, a small section was not coated to allow the analyzing light to enter and leave the cell. Prisms were cemented to the back of the electrode over these uncoated sections using Lensbond optical cement (Edmund Scientific Co., Barrington, NJ). The cell spacing was fixed using teflon spacers.

A 7 mm dia. glass tube approximately 25 cm long for filling and outgassing was sealed to the edge of the cell midway between the two ends in the plane perpendicular to the paper as indicated by the dashed circle. The entire cell was made vacuum tight using Ultrex vacuum epoxy (Perkin Elmer, Reston, VA). The Ag/AgCl reference electrode and the Pt counter electrode were sealed in the filling tube, the former ca 1 mm from the edge of the working electrode and the latter ca 15 cm away. The uncompensated resistance of a representative cell is ca 160 ohms. A vacuum stopcock at the end of the filling tube leads to a 100 ml bulb containing the MB solution, and a sidearm between the bulb and the stopcock permits outgassing on a vacuum line.

After the solution in the 100 ml bulb was outgassed by 7 freeze-pump-thaw cycles at a pressure below 10^{-5} torr, the sidearm was sealed off, and the stopcock was closed to prevent the solution from entering the cell. The cell was positioned in the light path and the angle of incidence of the beam on the prism was adjusted to within ± 0.5 minutes of arc using a precision rotation unit (Ealing Optical, Cambridge, MA). Such accuracy is necessary for quantitative

results. The angle of reflection at the electrode surface (α) was calculated from the angle of incidence on the entrance prism and the corresponding refractive indices. The stopcock was then opened to fill the cell compartment. The analyzing light was a 0.95 mw He/Ne laser (632.8nm) and the light intensity of the exit beam was monitored using a 9558B photomultiplier tube (EMI Corp., Los Angeles, CA). The entire unit was in a lightproof box.

The electrode potential was controlled with a PAR 170 Electrochemistry System and a Biomation 1010 waveform recorder (Gould, Santa Clara, CA) and an X-Y plotter were used to record optical transients. The reference beam intensity for absorbance calculations was taken as the steady state PM output which was reached ca 30 seconds after application of -0.7V to the working electrode.

Methylene blue (Eastman) was purified by successive extractions with benzene (15) from a slightly ammoniacal solution followed by two recrystallizations from 50% aqueous ethanol. The supporting electrolyte was 0.1 $\underline{M}$ KCl buffered to pH 7 with $10^{-3}\underline{M}$ $H_2PO_4^-/HPO_4^=$.

RESULTS AND DISCUSSION

To evaluate the MSR cell, we have compared the initial absorbance and the transient absorbance to the behavior predicted by Equations 4 and 5. All results refer to a cell 120 μm thick and 4 cm long, and a wavelength of 632.8nm.

The angular dependence of the initial absorbance of a $4.0 \times 10^{-6}\underline{M}$ MB solution is summarized in Table I, which reports calculated absorbance, measured absorbance and the calculated number of reflections for angles ranging from 30° to 60°. In general, the observed and calculated absorbances agree reasonably well, but the absorbance values are somewhat higher than the calculated values at angles above 45°. We do not understand the reason for this deviation.

Absorbance transients for the reduction of MB and the reoxidation of LMB secured with α equal to 45° are plotted $\underline{vs}$ $t^{\frac{1}{2}}$ in Figures 2 and 3. The transients

obey the theory well for bulk concentrations of MB between 6×10^{-6} M and 5×10^{-7} M, the lowest concentration studied. When the bulk concentration of MB exceeds 6×10^{-6} M, the limited solubility of LMB in the supporting electrolyte causes the transient response to deviate from ideality.

Transients for the reduction of MB at initial concentrations from 5×10^{-7} M to 1×10^{-5} M generated by stepping the potential from +0.1V to -0.7V are plotted against $t^{\frac{1}{2}}$ in Figure 2. Although minute changes in surface reflectivity could lead to serious errors in measurements, over the potential range of interest, blank experiments without the dye showed no detectable absorbance changes during electrolysis. For MB concentrations up to and including 8×10^{-6} M, the transients agree well with Equation 5. The plots are linear from 10ms to ca 3s, the slopes being proportional to the bulk concentrations of MB. At longer times, the plots become nonlinear as the diffusion is no longer semi-infinite. Also, for each transient, the absorbance at zero time obtained by extrapolation is directly proportional to the bulk concentration of MB and it agrees well with the absorbance of 4×10^{-6} M MB at 45° is 1.28 in Table I, and the transient absorbance at zero time is 1.27. The diffusion coefficient of MB calculated from Equation 5 is $4.7 \times 10^{-6} \text{cm}^2 \text{sec}^{-1}$, which corresponds reasonably well to the polarographically measured value of $4.1 \times 10^{-6} \text{cm}^2 \text{sec}^{-1}$ (16).

In contrast to the ideal transients observed at lower MB concentrations, the transient for 1×10^{-5} M MB begins to deviate from theory after ca 0.5 seconds, and the deviation increases progressively with time. We attribute this artifact to precipitation of LMB on the electrode surface. Pergola et al (16) have shown that the solubility of LMB is approximately 7×10^{-6} M, a concentration that is quickly exceeded in the reduction of 1×10^{-5} M MB. Visual observation of the MSR cell during the experiment confirms that LMB precipitates. Shortly after application of the cathodic potential step, the beam at the exit prism becomes noticeably more diffuse, indicating an increase in scattering which does not occur

at the lower MB concentrations.

Transients for oxidation of LMB at concentrations from $5 \times 10^{-7} \underline{M}$ to $1 \times 10^{-5} \underline{M}$ generated by first reducing MB for 30 seconds at $-0.7V$ and then stepping the potential to $+0.1V$ are plotted $\underline{vs}$ $t^{\frac{1}{2}}$ in Figure 3. Blank experiments without MB gave no detectable absorbance transients. For MB concentrations up to and including $6 \times 10^{-6} \underline{M}$, the transients conform well to Equation 4. From 10ms to $\underline{ca}$ 3 seconds, the plots are linear with slopes proportional to the bulk concentrations of LMB and they extrapolate to the origin. The diffusion coefficient of LMB, calculated from Equation 4, is $4.0 \times 10^{-6} cm^2 sec^{-1}$. Although the transients for $8 \times 10^{-6} \underline{M}$ and $1 \times 10^{-5} \underline{M}$ LMB are linear, they extrapolate to finite absorbance at zero time, an effect we attribute to the precipitation of LMB on the electrode surface. Because the precipitate causes scattering of the light beam, it is not possible to define the true absorbance at the beginning of these transients, but it is significant that after 10 ms, both transients have slopes that correspond to a LMB concentration of $\underline{ca}$ $7 \times 10^{-6} \underline{M}$, i.e., a saturated solution of LMB (16). Apparently the precipitated LMB is reoxidized within the first 10ms, after which the transient is governed by diffusion of LMB in the usual manner.

The electrodes in these experiments were gold, but there is no reason to believe that other conductors or semiconductors would not be suitable provided that the surface is flat, nonabsorbing and highly reflective. Preliminary experiments with both platinum foil and platinum films sputtered on glass indicate that these materials are satisfactory for MSR cells. Attempts to replace the laser with a focused xenon lamp gave greatly decreased reproducibility, presumably due to optical beam divergence within the cell. We believe that the use of a laser as the analyzing source is probably necessary for this reason. In addition to their use in monitoring reactants and products in electrochemical processes, MSR cells may prove useful for detecting short-lived intermediates. For such applications, minimizing the cell thickness and increasing the angle of the light beam relative to the electrode surface should prove advantageous in maximizing the sensitivity.

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ACKNOWLEDGEMENT

Table I

Influence of Angle of Illumination on Steady State

Absorbance of MB in MSR Cell

| α, Degrees | Reflections | Absorbance | |
		Calc.	Meas.
30	192	1.03	1.01
35	233	1.09	1.13
40	280	1.17	1.09
45	333	1.27	1.28
50	397	1.40	1.44
55	476	1.56	1.68
60	577	1.80	1.97

Conditions:

MB Conc; $4 \times 10^{-6} \underline{M}$

Cell Length; 4.0 cm.

Cell Thickness; 120μm

$\epsilon_{MB} = 56000 \ M^{-1} cm^{-1}$ (632.8nm)

FIGURE CAPTIONS

Figure 1.   Cross Section of the Multiple Specular Reflection Spectroelectrochemical
Cell. Not to Scale. The dotted circle indicates the filling tube.

Figure 2.   Absorbance $\underline{vs}$ $t^{\frac{1}{2}}$ for the Reduction of Methylene Blue at Concentrations
of $0.5 \times 10^{-6}\underline{M}$ to $10 \times 10^{-6}\underline{M}$. Numbers at the right hand border equal
MB concentrations x 10^6.

Figure 3.   Absorbance $\underline{vs}$ $t^{\frac{1}{2}}$ for the Oxidation of Leucomethylene Blue at Concentra-
tions of $0.5 \times 10^{-6}\underline{M}$ to $10 \times 10^{-6}\underline{M}$. Numbers at the right hand border
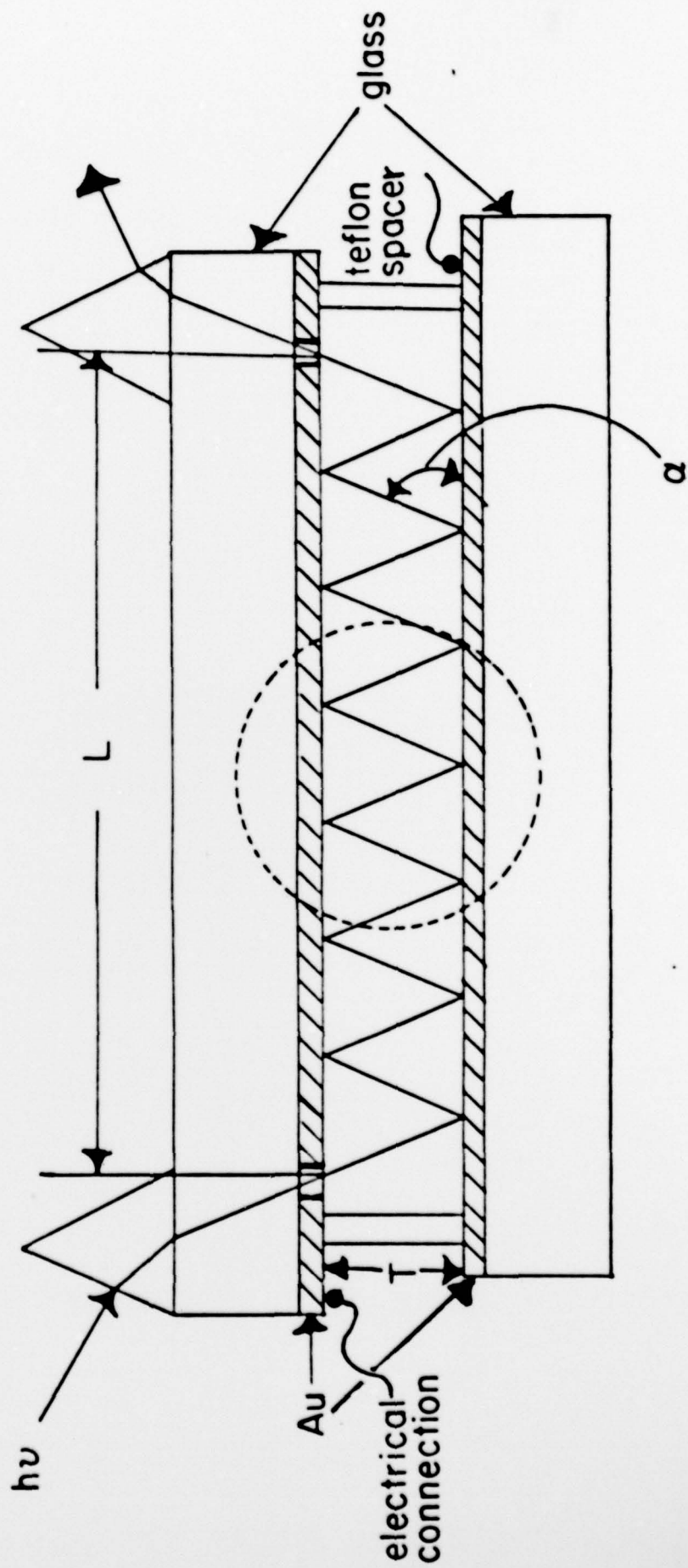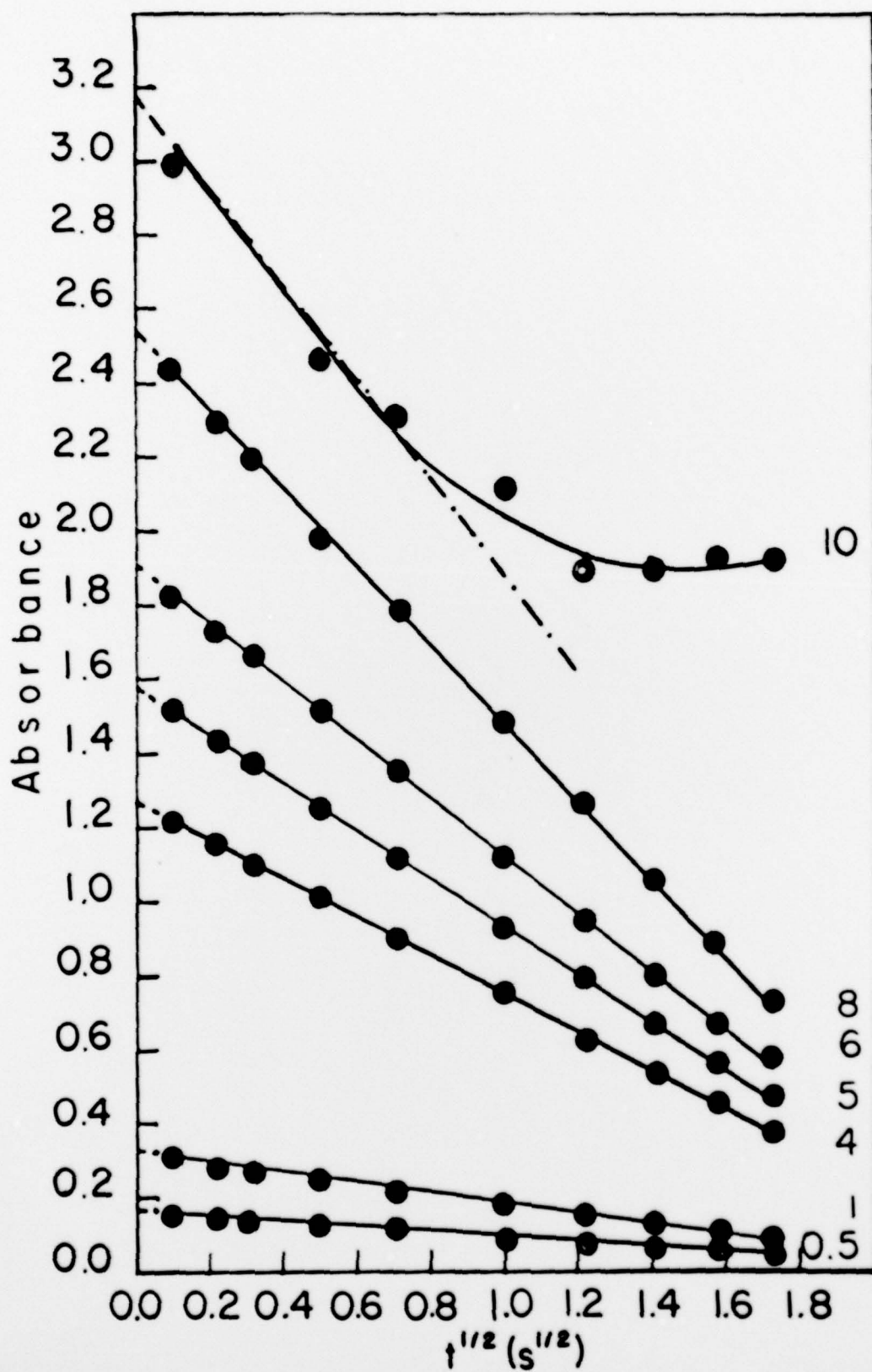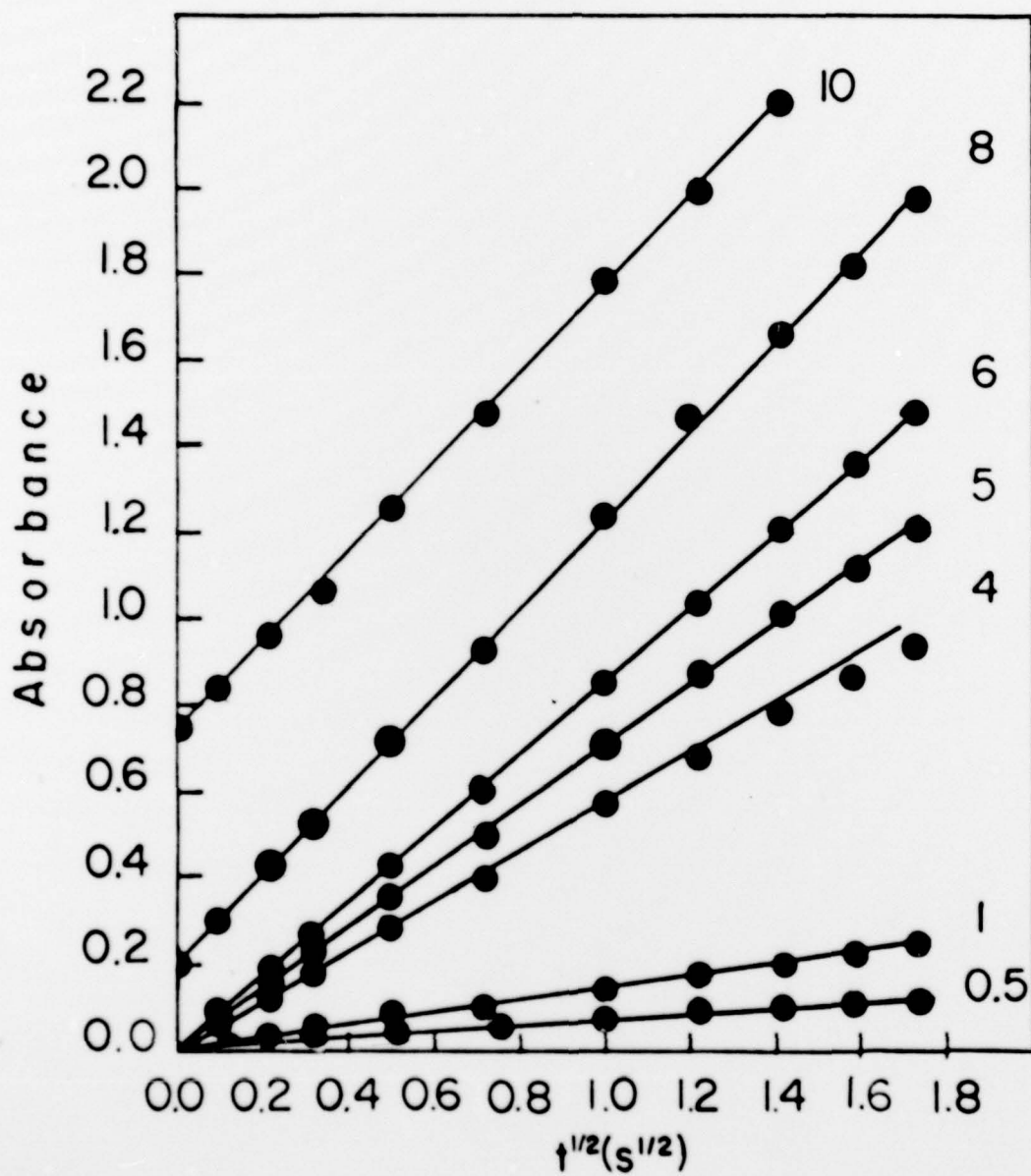equal MB concentrations x 10^6.

FIGURE 1

FIGURE 2

FIGURE 3

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